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Reactions between Acetylene and Propylene. (II)

The Reaction Mechanism

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From the results of the product analysis described in the previous paper, the author has proposed a radical mechanism, and tried various experiments to support the theory.

There are many reports on the catalytic pyrolysis of acetylene or propylene, and some of them described their reaction mechanisms²⁾⁻⁵⁾. They concluded that these reactions seem to proceed through radical mechanisms. The pyrolysis of the mixture of acetylene and propylene, however, has not been studied so far. As reported in the previous paper¹⁾, the author has studied the catalytic pyrolysis of this mixture and reported the effects of the catalysts on the products. In the present paper, the mechanism of this reaction is proposed.

RESULTS AND DISCUSSION

The effects of the catalysts on the compositions of the detectable products, hydrogen, methane, ethane, ethylene, propane, 1-butene, 2-methyl-1-butene, and methyl chloride have been reported in the previous paper and are shown in Figs. 1-8.

1) **Formation of methane.** As shown in Figure 3, the formation of a large amounts of methyl chloride was observed with the copper chlorides-alumina catalysts at low temperature, namely when the catalysts were fresh. It appears that

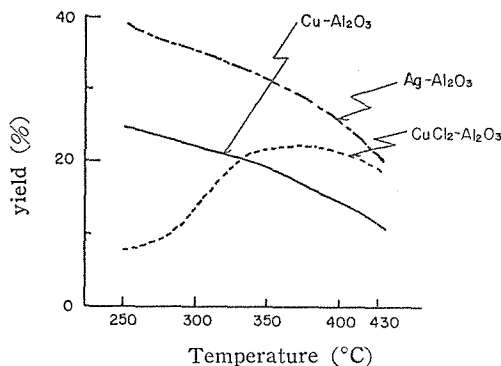


Fig. 1. The effects of the catalysts on the formation of hydrogen.

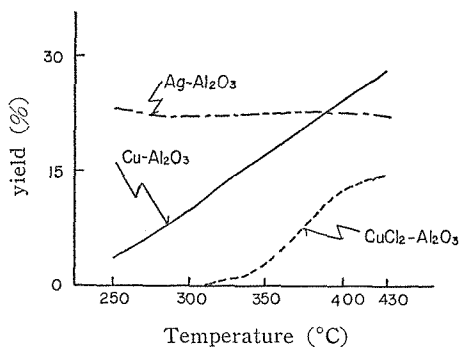


Fig. 2. The effects of the catalysts on the formation of methane.

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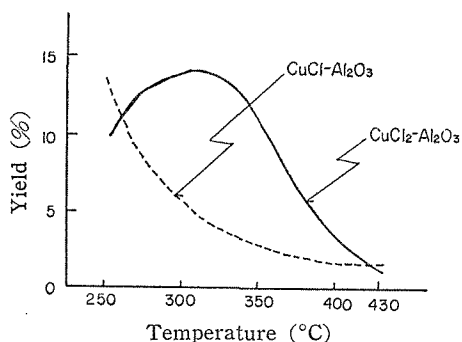


Fig. 3. The effects of the catalysts on the formation of methyl chloride.

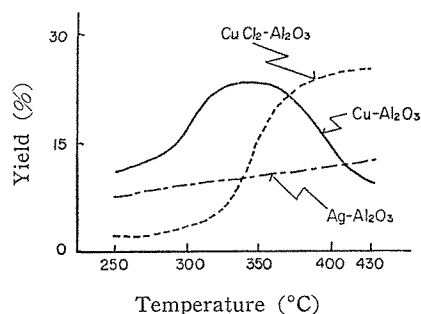


Fig. 4. The effects of the catalysts on the formation of ethane.

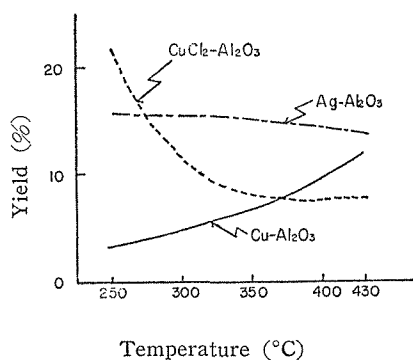


Fig. 5. The effects of the catalysts on the formation of ethylene.

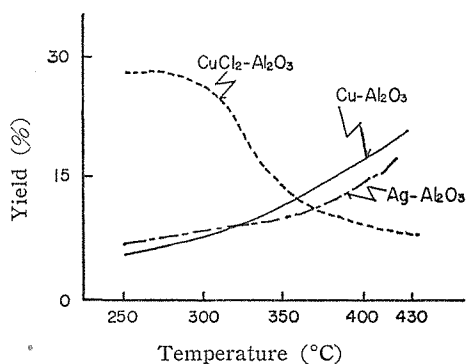


Fig. 6. The effects of the catalysts on the formation of propane.

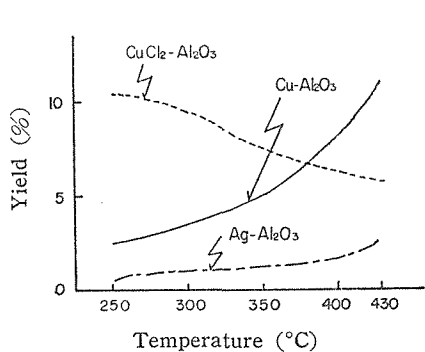


Fig. 7. The effects of the catalysts on the formation of 1-butene.

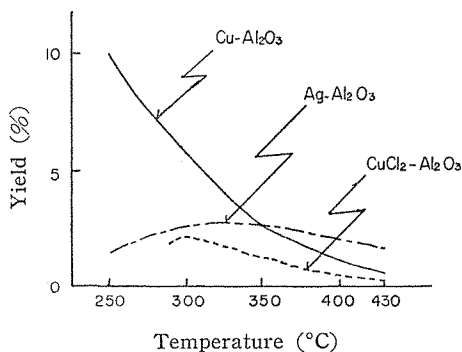
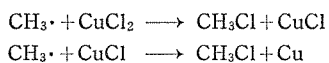


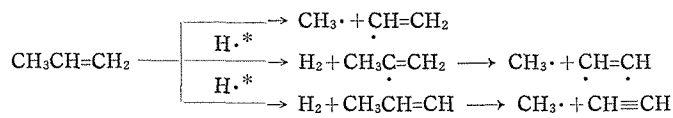
Fig. 8. The effects of the catalysts on the formation of 2-methyl-1-butene.

this methyl chloride was formed by the reaction of methyl radical with copper chlorides by the following equations.

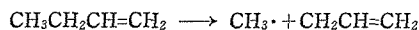


These are the same type of reactions as those proposed by Bamford⁶⁾, and this fact suggested the existence of free radicals. Methyl radicals can be assumed to

be produced from propylene according to the following equations.

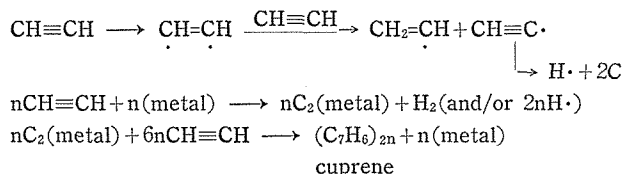


It can be formed also from 1-butene according to the following reaction scheme which will be discussed later.



Methyl radical thus produced reacts with hydrogen or hydrogen atom (described later) to form methane. From these reasons, the amounts of methane formed are large when the reactions proceed without the radical trapping reagent. In the presence of these reagent such as toluene²⁹ or nitrogen oxide³⁰, however, hydrogen atom is trapped by toluene or nitrogen oxide, and decomposition of propylene by the hydrogen atom was retarded in the present results at the relatively low temperatures. The amount of methyl radical, therefore, became small and the volume of methane formed decreased.

2) **Formation of hydrogen.** It appears that the amounts of hydrogen and saturated lower hydrocarbons depend on the extents of the reaction percents of acetylene and independent of the existence of the radical trap. It was observed that large amounts of carbon and cuprene deposited on the catalyst after the reaction. Therefore, hydrogen and/or hydrogen atom is thought to have been produced by the following equations.



Other possibility of the hydrogen formation is that from the radicals which is produced from the decomposition of propylene, but it seems that the volume of hydrogen by this reaction should be smaller than that by the decomposition of acetylene.

The existence of hydrogen atom was confirmed by Melville's method⁹⁾. This method is a quantitative one, but was used qualitatively here. The author's result was the same as Melville's. It was observed that the color of molybdenum trioxide changed from light yellow to blue by the reaction (by the reduction with hydrogen atom). The reaction products are shown in Table 1. Thus the existence of radical was confirmed, and further by the experiments with toluene carrier and nitrogen oxide. The former is Szwarc's method¹⁰⁾, which was used for the proof of the existence of radicals in the pyrolysis of alkyl benzenes. The result obtained here was the same as Szwarc's in the experiments to confirm the formation of dibenzyl. These facts show the existence of radicals in the reaction. The reaction products are shown in Table 2. The latter is Hinshelwood's method¹¹⁾

* This hydrogen atom is discussed in the next part.

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Table 1. Reaction products in the presence of copper-alumina and molybdenum trioxide-alumina catalyst.

Reaction temperature (°C)	250	300	350	400	430	
Conversion (Vol. %)	{ acetylene	80.5	86.5	90.0	94.5	98.5
	{ propylene	64.0	68.5	73.0	76.5	80.5
Products (Vol. %)	{ hydrogen	21.8	25.6	28.3	28.0	26.3
	{ methane	12.1	25.2	28.3	28.7	29.0
	{ ethane	4.6	1.7	0.6	0.3	0.2
	{ ethylene	14.6	18.4	21.2	26.1	26.9
	{ propane	19.0	14.4	11.5	10.4	8.2
	{ 1-butene	0	0	0	0	0.6
	{ 2-butene	0	0	0.2	0.3	0.4
	{ 1, 3-butadiene	0	0	0	0.9	1.1
	{ 2-metyl butane	0	0	0.2	0.5	0.6
	{ 2-methyl-1-butene	0	0	0	0	0.3
	{ 3-methyl-1-butene	8.1	2.8	2.4	1.6	1.2
	{ 1-pentene	0	0	0	0	1.8
	{ 2-pentene	0	0	0	0	0.7
	{ 1, 4-pentadiene	0	0	0	0	0.2
	{ isoprene	0	0	0	0	0.7
	{ 2, 3-dimethyl-1-butene	0	0	0	0	0.2
	{ hexenes	19.8	11.8	7.2	3.5	1.7
Volume change (%)	9.4	16.6	23.4	29.6	43.6	

Table 2. Reaction products in the presence of copper-alumina catalyst with toluene vapor.

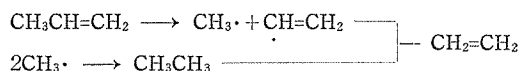
Reaction temperature (°C)		250	300	350	400	430
Conversion (Vol. %)	{ acetylene	76.5	79.5	82.5	87.5	91.5
	{ propylene	41.5	45.0	50.5	58.5	65.5
Products (Vol. %)	{ hydrogen	18.3	18.8	20.8	22.1	20.3
	{ methane	4.4	9.1	11.8	21.2	21.1
	{ ethane	14.1	13.5	12.3	10.5	10.6
	{ ethylene	25.2	25.2	24.9	21.8	24.0
	{ propane	17.8	16.9	15.8	13.1	13.2
	{ 1-butene	2.0	3.9	3.9	4.2	5.1
	{ 2-butene	3.8	3.3	2.8	1.9	1.5
	{ 1,3-butadiene	0.7	0.6	0.4	0.2	0.1
	{ 2-methyl butane	0.4	0.8	1.7	2.0	2.0
	{ 2-methyl-1-butene	2.3	0	0	0	0
	{ 3-methyl-1-butene	3.8	2.3	1.4	0.6	0.5
	{ 1-pentene	3.2	2.9	2.5	1.5	1.5
	{ 2-pentene	3.8	2.5	1.8	0.7	0.6
Volume change (%)		17.2	25.7	42.8	75.3	91.1

Table 3. Reaction products in the presence of silver-alumina catalyst with nitrogen oxide.

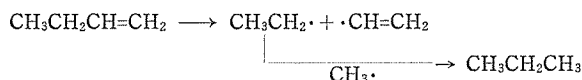
Reaction temperature (°C)		250	300	350	400	430	
Conversion (Vol. %)	{ acetylene		62.5	67.0	71.5	73.5	
	{ propylene		13.5	19.5	23.5	26.5	
Products (Vol. %)	{	hydrogen		14.5	15.8	18.6	21.0
		methane		8.7	8.9	10.2	11.3
		ethane		4.4	3.7	3.1	2.5
		ethylene		13.3	15.6	17.5	19.5
		propane		50.7	49.2	44.4	40.4
		1-butene		0.3	0.4	0.6	0.7
		2-butene		0.3	0.2	0.1	0
		1, 3-butadiene		0.2	0.3	0.4	0.4
		2-methyl butane		0.5	0.4	0.4	0.3
		2-methyl-1-butene		0.2	0.1	0.1	0
		3-methyl-1-butene		1.3	1.2	1.3	1.4
		1-pentene		2.1	1.7	1.5	1.2
		hexenes		3.4	2.6	1.9	1.4
Volume change (%)			-1.2	4.5	8.2	9.6	

and the results are shown in Table 3. The reaction was retarded strongly and the main products were hydrogen, lower hydrocarbons which are thought to be the primary decomposition products and propane which is thought to be produced from above products and/or propylene. It is probable that hydrogen was produced mainly by the decomposition of acetylene, since a large amounts of hydrogen was produced in spite of the existence of such radical trapping reagents.

3) **Formation of ethane and ethylene.** The most probable source of ethane appears to be the reduction of acetylene and the recombination of two methyl radicals which are formed by the decomposition of propylene. Ethylene is produced by the same decomposition.



4) **Formation of propane.** It is possible that propane is formed by the equation below. Since the amount of 1-butene was very small, however, the main reaction of the propane formation must be the reduction of propylene.

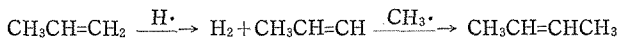


5) **Formation of C₄ hydrocarbons.** It is possible that 1-butene is produced by the partial reduction of acetylene dimer. Considering that the volume of hydrogen depends on the extent of the conversion of acetylene and large amounts of carbon and cuprene were produced, however, 1-butene must be produced mainly by the following mechanism.

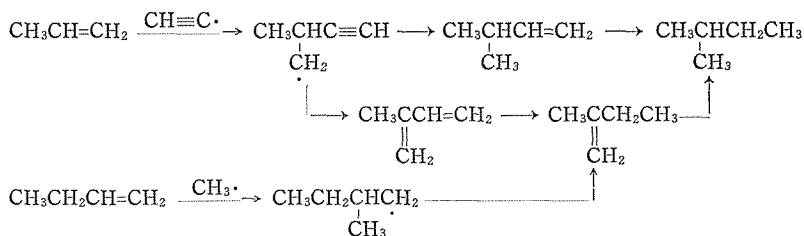
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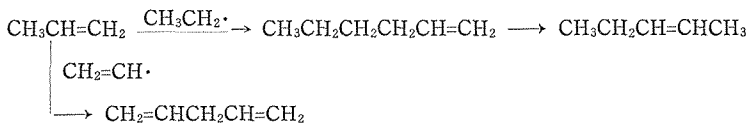
The formation of 1,3-butadiene can be explained by this mechanism also. 2-Butene appears to be produced by the isomerization of 1-butene and/or by the following reaction from propylene.



6) **Formation of C₅ hydrocarbons.** It seems that the compounds having the isoprene skeleton such as 2- and 3-methyl-1-butene and isoprene are produced by the following mechanisms, and reduced to 2-methyl butane.



Pentenes are probably formed by the following reactions.



7) **Formation of hexenes.** Hexenes appear to be produced by the following mechanism besides the reduction of acetylene trimer and the propylene dimer.



The formation of higher hydrocarbons than C_4 (including C_4 hydrocarbons) can not be explained by any kind of one step reaction. The formation of these compounds was suppressed by the presence of the radical trapping reagents, especially by nitrogen oxide as is shown in Table 3.

As is described above, it seems that the radicals produced by the primary decomposition combine together and/or react with the raw materials to form many radicals and many compounds, as was pointed out by Egloff^{23,3)}. Thus the mechanism of the reaction between acetylene and propylene seems to be summarized in the scheme shown in Fig. 9.

EXPERIMENTAL

1) **Reaction with toluene carrier.** The catalyst (copper-alumina) was the same as described in the previous paper¹⁾. The apparatus was fitted with the device to mix the toluene vapor with the feed gas (Fig. 10). The temperature of toluene was kept at 105° and the ratio of toluene vapor and the feed gas was one to five by volume. Procedures and analytical methods of this and the following experiments were the same as described in the previous paper. After the

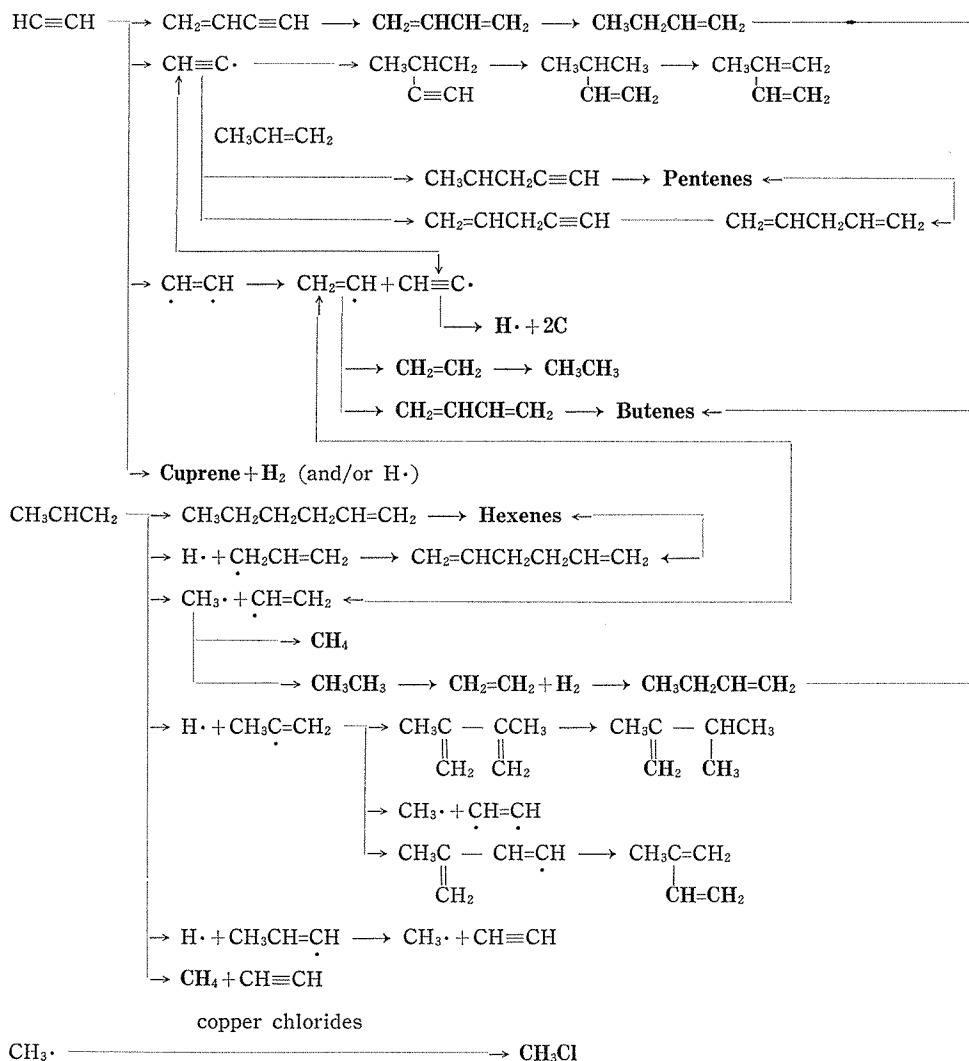


Fig. 9 Scheme of reaction mechanism.

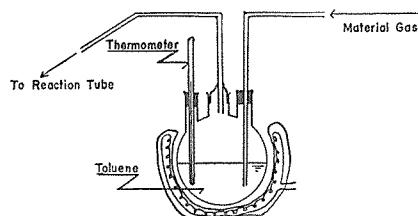


Fig. 10. The device to mix the toluene vapor.

reaction was stopped, toluene and dibenzyl were found in the liquid condensates. Dibenzyl was identified by its melting point and elementary analysis after a recrystallization from ethanol. (mp. 50–51°; Found: C 92.23; H 7.76, calcd. for $\text{C}_{14}\text{H}_{14}$: C 92.26; H 7.74%)

2) **Reaction with molybdenum trioxide.** The apparatus was the same as described in the previous paper¹⁾. Five cc. of the copper-alumina catalyst and then 5cc. of the molybdenum trioxide-alumina tablets* were placed in the reaction tube and glass-wool was inserted between the two kind of the catalysts. These procedures were repeated successively to fill up the reaction tube. The color of the molybdenum trioxide tablets which was light yellow before the reaction, changed to blue after the reaction.

On the surface of the copper-alumina catalyst, carbon and cuprene were observed (10g.). By the elementary analysis, the ratio of carbon and cuprene was found to be about 1 to 2 by weight. (Found: C 95.6; H 4.42. Calcd. for $(C_7H_6)_n$: C 93.26; H 6.71%) The formations of carbon and cuprene were observed in every cases.

3) **Reaction with nitrogen oxide.** The catalyst (silver-alumina) was the same as in the previous paper¹⁾. The apparatus was fitted with the device to introduce nitrogen oxide (Fig. 11). Nitrogen oxide in the gas holder (HN) was introduced by the flow of mercury (Hg) into the reaction tube (R) through the capillary (Cp). The rates were controlled by the flow rates of mercury (1ml./min.). The percentage of nitrogen oxide to material gas was 1.0%.

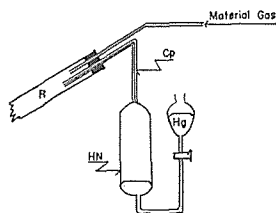


Fig. 11. The device to introduce nitrogen oxide.
(R: reaction tube; Cp: capillary; HN: nitrogen oxide gas holder; Hg: mercury)

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* The molybdenum trioxide-alumina tablets were prepared by the following method: Ammonium molybdate (15g.) was dissolved in 100ml. of 6*N*-nitric acid, and warmed to 50°. To this solution, 25g. of activated alumina tablet were added. This mixture was evaporated to dryness under reduced pressure. The tablets were washed with 1l. of water thoroughly and packed in the reaction tube and dried again at 200° for 2 hours in the stream of air.

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